The Mechanical Response of Materials and the Multiscale Simulation of Brittle Fracture in Silicon

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We describe a new linear scaling tight-binding molecular dynamics method for nonperiodic systems at finite temperature. We present a scheme for dynamical coupling of this tight-binding molecular dynamics to empirical potential molecular dynamics for use in multiscale simulations. This new coupling of length scales code is applied to the fracture failure of silicon. Unlike empirical potential simulations that show ductility, our simulations show crack propagation proceeding by cleaving bonds in sequence. This marks the first simulation that shows brittle fracture in a realistic model of silicon. Differences in empirical potential and tight-binding descriptions of atomic bonding are discussed in the context of fracture.

I. Introduction

The mechanical response of a material to applied stresses or strains often involves physical processes on a wide range of length scales. Dislocations that evolve and move during plastic deformation are a common example. These topological defects extend over many lattice constants and have long range strain fields, yet the structure of the core at the atomic scale determines in large part the mobility of the dislocation, and thus the plastic response of the material. A more complex example is the fracture failure of materials, which has become the archetypal multiscale materials phenomenon. Here the effect of long-range elastic fields is focused on a few interatomic bonds at the crack tip. On the shortest length scale, bonds at the crack tip are distorted and broken as the crack propagates. On the atomic to nanometer length scale, dislocations evolve and move, and voids may open. Elastic energy stored on length scales up to the dimensions of the system is slowly released. The importance of physical processes on a wide range of length scales makes accurate simulations of materials failure and fracture dynamics based on first principles calculations a challenge.

brittle-to-ductile transition has been seen. Similar results were obtained with the original CLS method,[5] which used a tight-binding scheme optimized for speed at the smallest length scales. At all temperatures fracture appears to be ductile. Fig. 1 shows a snapshot of a well-developed crack at low temperature. Narrow tendrils of disordered lattice emanate from the crack surface and small voids appear. Careful tracing of lattice planes shows dislocations buried in the tendrils. In these simulations[2,5] the energy to fracture is some four times what is expected from the brittle-fracture threshold given by the energy balance argument of Griffith.

These results disagree with experiment,[6] where at low temperatures the energy to fracture is close to the Griffith criterion and the fracture is brittle. This calls into question the accuracy of empirical potentials for predicting the nature of fracture, at least in materials with strong covalent bonds. Two microscopic mechanisms have been suggested for brittle fracture. The first is intuitively obvious; the crack propagates by cleaving the bonds between two adjacent atomic planes. The second was proposed by Rice.[7] Based on a comparison of the ratio of surface energy γ_s to the unstable stacking fault energy γ_{us} for various fcc and bcc metals and for diamond cubic semiconductors, Rice argued that it is favorable for dislocations to form in silicon. To reconcile this with the observation of brittle fracture in silicon, Rice proposed that dislocations are created at the crack tip and near crack surfaces, but do not contribute to plasticity because they are not mobile. It is natural to expect that at higher temperature the dislocation mobility would increase, suggesting a possible mechanism for the brittle-to-ductile transition.

To better understand why the results of simulations are in apparent disagreement with experiment, we consider the description of forces on atoms on the smallest length scales. We describe a new tight-binding molecular dynamics (TBMD) method that enables a more accurate description of atomic bonding and the forces on atoms arising from electronic degrees of freedom. We present a method for coupling the TBMD to empirical potential molecular dynamics to construct an improved *coupling of length scales* simulation methodology that is more accurate on the smallest length scales. We apply this simulation tool to the fracture of silicon at low temperature and observe brittle fracture. Simply increasing the temperature has not, however, shown ductile fracture, suggesting that the mechanism for the brittle-to-ductile transition may be a kinetic transition or involve the interaction of the propagating crack with crystalline defects or microstructure.

II. Simulation Methodology

The central ideas behind the *coupling of length scales* methodology and its original

1. The *Coupling of Length Scales*: a Brief Summary

To simulate crack propagation and other phenomena that span many length scales, we use the CLS approach developed by Abraham, Broughton, Bernstein, and Kaxiras.[5] A CLS simulation is actually several concurrent simulations. Each simulation uses a different methodology, and each methodology is chosen according to the need for an accurate and economical physical description on a particular length scale. A central feature of CLS is that a simulation on given length scale is coupled to a simulation on the next larger or smaller length scale in such a way that dynamical information is freely exchanged between different regions. The utility of this approach depends on the existence of a domain decomposition in which it is possible to identify regions where physical descriptions of different accuracy are needed. For crack propagation, such a rough domain decomposition can be identified: electronic scale resolution at the bonds of the crack tip, atomic scale resolution in the process zone, and longer length scale resolution – according to the shortest wavelength elastic waves that are important – outside of the process zone.

For simulations of very large systems, finite element continuum mechanics is used to describe the long-ranged elastic fields far from the crack tip. In the process zone near the crack tip, the trajectory of each atom is tracked with molecular dynamics, using an empirical potential to compute the interatomic forces. In a small region at the crack tip, forces on atoms are computed with a formulation that uses quantum mechanics to explicitly describe the electrons that participate in the bonding of atoms. In this work, a tight-binding description of the electrons strikes a balance between computational economy and accuracy. The methodologies on different length scales are seamlessly coupled in 'handshaking' regions. The reader is referred to other works where 'handshaking' in the original CLS has been described in greater detail.[5] This work focuses on a significant improvement over the original CLS method; it focuses on the physical description at the smallest length scales where a quantum mechanical description of highly directional covalent bonds appears necessary to properly determine the nature of fracture in silicon. The simulated systems are small enough to be described entirely atomistically, without a continuum mechanics region. In the following we describe a TBMD method and a strategy for coupling TBMD to empirical potential molecular dynamics, and apply it to the demanding problem of fracture.

2. Forces on Small Length Scales and Tight-Binding Molecular Dynamics

In molecular dynamics, Newton's classical equations of motion are integrated over time

describe an iterative inversion method (IIM) for calculating forces for tight-binding molecular dynamics.

We identify a region where electronic degrees of freedom must be handled quantum mechanically. It is a good approximation to consider this subsystem to be in thermodynamic equilibrium and able to exchange electrons with the electronic reservoir composed of the rest of the system. The force on an atom in the subsystem can be obtained by differentiating the grand thermodynamic potential of the subsystem with respect to atomic position at fixed chemical potential. After formal manipulation, the force on atom α, F_α , can be expressed[8] in terms of a Green's function matrix **G**, and tight-binding Hamiltonian and overlap matrices **H** and **S**,

$$F_a = -\frac{\partial \Omega\left[T, m, \{r_j\}\right]}{\partial r_a} = 4\,\mathrm{Re}\sum_{i=1}^{N_{\mathrm{pokes}}} \mathrm{Tr}\left[a_i \mathbf{G}(z_i)\left(\frac{\partial \mathbf{H}}{\partial r_i} - z_i \frac{\partial \mathbf{S}}{\partial r_i}\right)\right]. \qquad (1)$$

Here the matrix elements of **G**, **H**, and **S** are labeled by position and wavefunction indices, Ω is the grand thermodynamic potential, and a_i are residues of an approximate Fermi function[9] evaluated at the poles of that function in the upper half plane z_i.

The main computational work in evaluating the force equation lies in calculating the matrix **G**, which is simply related to **H** and **S** through the expression

$$(z\mathbf{S} - \mathbf{H})\mathbf{G} = \mathbf{1}, \qquad (2)$$

where z is a complex variable and **1** is the identity matrix. We use an iterative biconjugate gradient algorithm[8,10] to invert Eq. 2. This method has two important features: (1) arbitrary matrix elements of **G** can be fixed to particular values during the iteration process, and (2) the computational effort in solving Eq. 2 scales linearly with the number of atoms in the tight-binding subsystem. The central problem in practical applications of this formula to multiscale problems lies in handling the boundary where the coupling to empirical potential molecular dynamics occurs. It is possible to choose the boundary of the tight-binding region to be sufficiently far from the crack tip that the *local* environment of the atoms on the boundary resembles an ideal lattice. However, there is, in general, no symmetry operation that connects two well-separated atoms on the boundary. The IIM method allows these kinds of nearly ideal lattice boundary conditions to be implemented with relative ease. Boundary atoms form a 6 Å wide region. Matrix elements of **G** for boundary atoms are constrained to values for atoms in ideal lattices with the same orientation and lattice spacing. This method has been applied to forces on atoms around vacancies,[8] to compute forces in a tight-binding molecular dynamics simulation of the temperature dependent dislocation core structure,[8] and in the simulation of fracture of silicon.[11,12] The application of boundary conditions on **G** is essentially

III. Simulation of Fracture Failure of Silicon

1. Descriptions of Bonding in Silicon

A materials-specific model with predictive power for not only the onset, but also the dynamics of fracture, requires an accurate description of electronic bonding. While the most accurate description of electronic bonding is obtained from *ab initio* density functional theory based calculations, these methods are computationally expensive. Here we use a minimal basis tight-binding description as a compromise between speed and accuracy. Because the accuracy of tight-binding methods depends on their functional form, as well as on the set of experimental data and *ab initio* calculations included in the construction of a specific tight-binding model, we are in the process of exploring fracture properties of several tight-binding models. Here we focus on two nonorthogonal minimal basis models. The first[13] (BK-TB) is based on the extended Huckel approach. The second[14] is based on the NRL-TB method. Both models use an sp^3 basis.

While both models provide a quantum mechanical description of covalent bonding, they differ in their functional forms and in the structures to which they were fit. The BK-TB model uses the conventional definition of the total energy as a sum of the occupied electronic eigenvalues and a pairwise repulsive potential. The fit included total energies of bulk lattices and defects, and the model has been shown to accurately reproduce bulk properties of silicon in the diamond crystal structure, energetics of point defects, surfaces, amorphous structures, and other 'distorted' geometries. The NRL-TB method shifts the on-site energies by an environment dependent term that replaces the conventional pair repulsion. This model was fit to a small number of bulk lattice cohesive energies and electronic structure information. It accurately reproduces a large set of materials properties, including elastic constants and phonon frequencies, point defect formation energies, surface energies, and surface reconstructions.[15] This model also reproduces the correct sequence of energies for adatom configurations on the (111) surface of silicon. Both models appear to give a good account of the physics of bonding in silicon, but they are likely to differ in the way they describe highly distorted and breaking bonds.

2. Tight-Binding and Brittle Fracture

Simulations were performed for a 400Å X 250Å X 12Å slab containing about 50000 atoms described by empirical potentials and about 1000 atoms described by tight-binding. The configuration of atoms is shown in Fig. 2. A seed crack was formed by removing part of a double row of silicon atoms as shown. A constant displacement was applied to

formation of dislocations during the course of the simulation. The crack speed can be determined from the rate of advance of the sequence of breaking bonds and is found to be ~2/3 of the Rayleigh speed. The Rayleigh speed is the speed of surface elastic waves and is the limiting speed of crack propagation according to linear continuum mechanics. Fig. 4 shows the crack velocity for simulations of fracture in comparison with the experiments of Hauch *et al.*,[6] plotted as a function of fracture energy G (not to be confused with the Green's function matrix **G**). While this is a work in progress, it can be seen that the simulation and experiment are in reasonably good agreement. What is most important to observe is that the critical energy to fracture (the abrupt rise in Fig. 4) in both simulation and experiment is nearly that predicted by the Griffith criterion. This is in contrast to simulations[2] using the Stillinger-Weber empirical potential that find the critical energy to fracture to be some four times the value from experiment, with a similarly large value for the EDIP empirical potential. To see directly the difference that the tight-binding region makes in the fracture simulation, Fig. 5 contrasts the fracture of silicon described purely by EDIP with the fracture of the EDIP model with an embedded tight-binding region. It is important to note that the pure EDIP description shows a significantly larger strain needed to fracture, and a blunt crack tip with indications of plastic deformation. Preliminary results from simulations using the NRL-TB model also show brittle fracture at 200K. So far, simulations performed at high temperature (1100K) have not shown ductile behavior for either model. These simulations show features suggestive of incipient dislocation formation that heal rapidly on the time scale of the simulation. This suggests that dislocation formation and ductility in the fracture of silicon may be a dynamical effect driven by fluctuations, and may appear on time scales longer than the total duration of any simulation using the IIM that we have performed so far. We are also investigating whether vacancies or interstitials might initiate or catalyze dislocation formation.

IV. Discussion

We have shown that brittle fracture may be observed in simulations of a model of silicon that uses a quantum mechanical description of the bonding between atoms at the crack tip. This is in contrast to all empirical-potential based descriptions of silicon. Holland and Marder[16] have recently shown that brittle fracture can be observed in empirical potential simulations when an 'inadvertently modified' Stillinger-Weber potential is used. This potential has a bond-bending term that is a factor of two larger than that of the true SW potential. This choice is not motivated by any physical consideration and the physical properties of 'inadvertently modified Stillinger-Weber' silicon differ significantly from those of real silicon. In contrast, our multiscale silicon model gives a realistic description of many properties of bulk and amorphous silicon as well as surface

To pursue this line of reasoning further, it is useful to quantitatively examine seemingly relevant physical properties as described by these models and to revisit the ideas behind Rice's original conjecture. The Table shows a number of material properties that are likely to be relevant to fracture. These include elastic constants and the surface and unstable stacking fault energies that Rice suggested govern the interplay between brittle and ductile fracture. There are no substantial, systematic differences between the empirical potentials and the tight-binding models despite the obvious qualitative differences in fracture simulations. In all cases the ratio of surface energy to minimum stacking fault energy is similar, and a comparison of the empirical potentials with the tight-binding models does not show a trend.

One reason that Rice's criterion does not predict the difference in behavior between the models is that it only compares two mechanisms: interplanar cleavage and blunting by dislocation emission. The mechanism that is seen in empirical potential simulations, crack tip amorphization, was not considered by Rice. Apparently for both the SW and EDIP empirical potentials this mechanism is the dominant one, although it is not seen in experiments. While this observation explains why the parameters considered by Rice do not reflect the differences between the fracture morphologies of the models, it does not suggest what are the relevant material properties that *do* distinguish them. One simple possibility is the range of interactions between atoms. The surface energy of a material can be measured by separating two slabs to form a new surface and integrating the force between the two slabs with respect to the separation. The force between the two slabs must decay to zero once they are farther apart than the interaction range. To integrate to the correct surface energy, shorter-range models (like SW and EDIP) must reach a higher peak force. This makes it much harder to separate the atoms of the planes being cleaved ahead of the crack in an EP simulation, as compared with tight-binding models that can have a longer interaction range, or with *ab initio* methods that can have even longer range. This effect is shown in Fig. 6, where we plot the energy and force on a sample under opening displacement in the (111) direction. The physical reason that many empirical potentials for silicon are short ranged is that the physics of the interaction between first neighbors, that of overlapping sp^3 hybrid orbitals, is qualitatively different from that of second neighbors. It is difficult to capture both in a single functional form, and so empirical potentials cut off the interaction between surfaces at an unphysically small separation.

V. **Conclusion**

We have improved the accuracy of the original CLS methodology to enable the

brittle fracture in a realistic model of silicon. We are currently investigating in more detail the origin of the very different fracture behavior observed in empirical potential and tight-binding descriptions of atomic bonding. We are focusing on whether our hybrid model of silicon exhibits a brittle-to-ductile transition with increasing temperature and on the importance of the description of atomic bonding in determining the nature of the transition. These investigations will no-doubt lead to further improvements to the CLS method. Of particular importance are the smallest length scales, where better coupling methods that can function seamlessly in 'handshaking' regions that deviate significantly from an ideal lattice geometry will lead to new applications such as the fracture of complex materials and metals.

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Table: Properties of silicon relevant to fracture according to different models.

	LDA	BK-TB	NRL-TB	SW	EDIP
C_{11} [GPa]	166	145	179	162	175
C_{12} [GPa]	63.3	84.5	73	81.6	65
C_{44} [GPa]	79.3	53.4	96	60.3	71
γ_s <111> [J/m^2]	1.7	1.5	1.6	1.45	1.64
γ_{us} (glide) [J/m^2]	2.51	4.0	3.6	4.78	3.24
γ_{us} (shuffle) [J/m^2]	1.84	1.9	2.3	1.38	2.16

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Figure Captions

Figure 1: Coupled Stillinger-Weber empirical potential and finite element continuum mechanics simulation of fracture in silicon. The left hand panel shows a large scale view of the crack, and right hand panel details the structure of a tendril of disordered material with a dislocation at its tip.

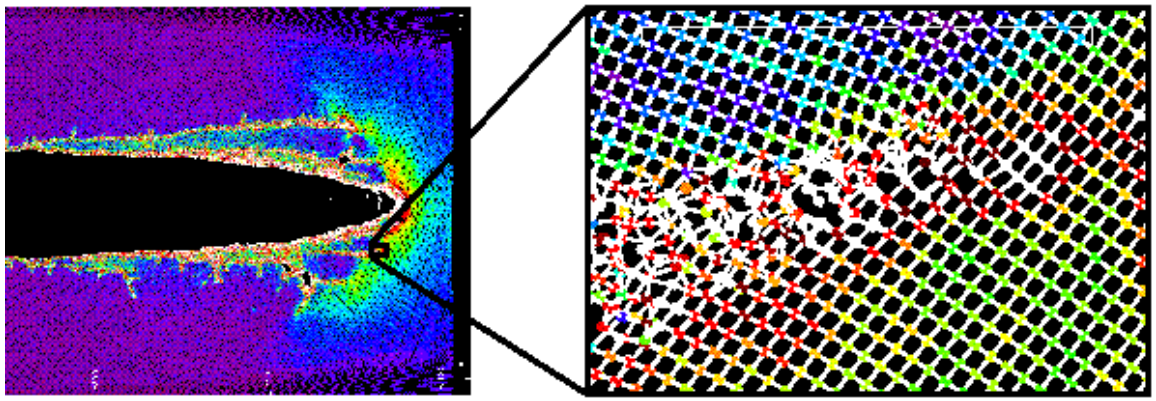
Figure 2: Detail of initial crack tip in the IIM simulation. Red atoms indicate the empirical potential region, green atoms indicate the tight-binding region, and blue atoms indicate the handshaking region.

Figure 3: Simulation snapshots showing the crack position at 4 times in a coupled empirical-potential and tight-binding simulation.

Figure 4: Crack speed as a function of energy release rate G for coupled EP-TB simulation (black squares) and experiment (red dots, from Ref. 6). Dashed lines indicate Griffith criterion of minimal energy release rate.

Figure 5: A comparison of crack tip features in a coupled EP-TB (left panels) and a pure EDIP (right panels) simulation.

Figure 6: Energy (left panel) and force (right panel) as a function of opening displacement along the (111) direction computed with the listed empirical potential and tight-binding models.



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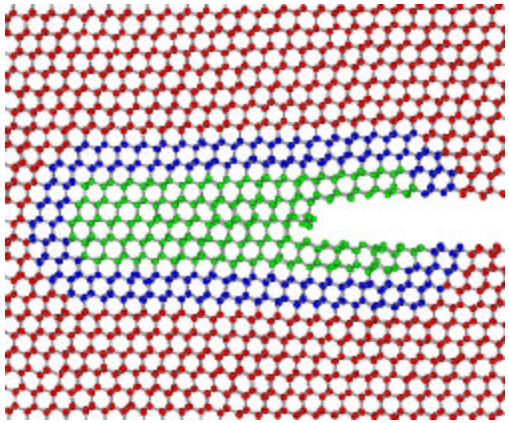

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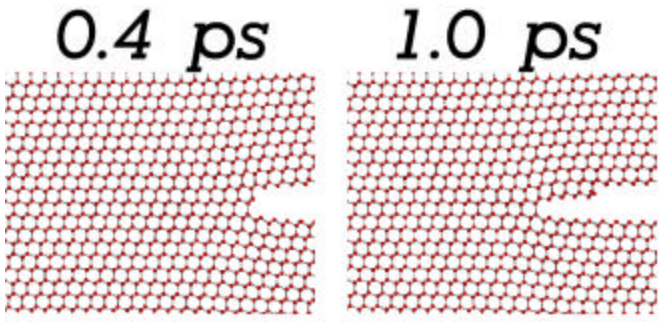

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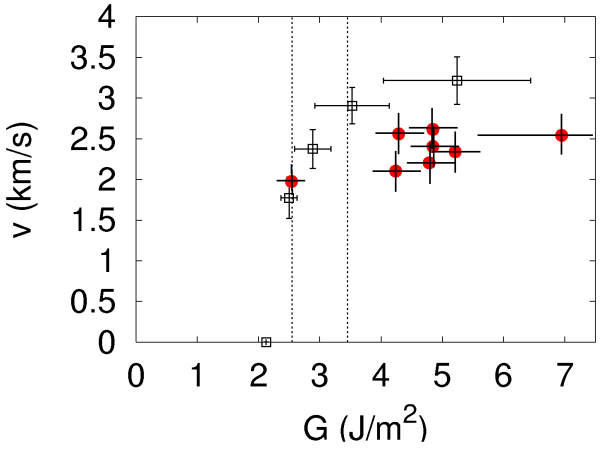

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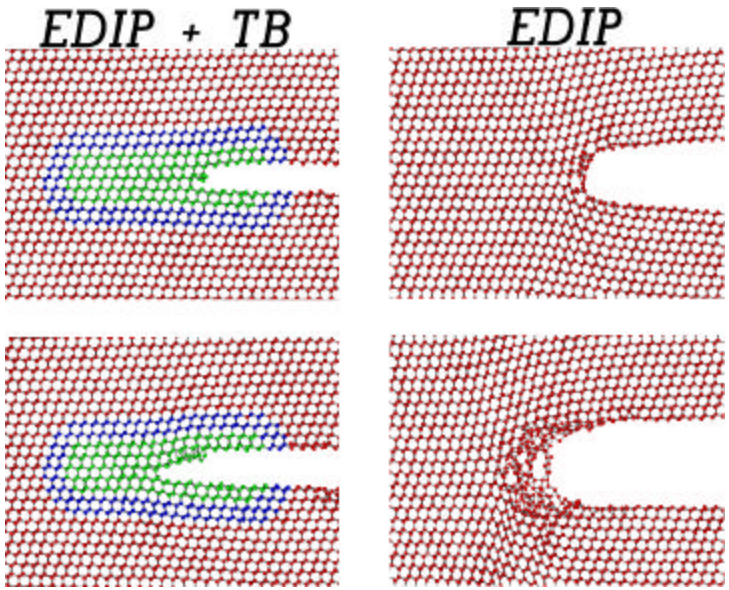

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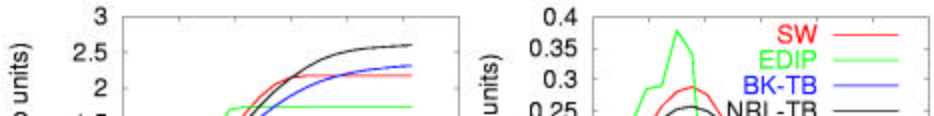

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